SOLUTION DENSITIES

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It has been shown¹ that with the first quantities of zinc sulphate added to a solution there is produced no change in the volume of the water solvent until a density of about 1.150 is reached, so that the density may be calculated by adding to the weight of one cc of water the weight of zinc sulphate contained in one cc, without making an error of more than two or three parts in one thousand. For densities higher than 1.150 one molecule of zinc sulphate displaces one molecule of water, giving rise to the linear expression —

$$\text{density} = \text{wt. water} + \text{wt. salt} - \frac{18}{161} (\text{wt. salt} - 0.150).$$

The break in the curve which appears to be so marked seems to have been entirely overlooked in the work of previous observers. For this reason we have considered it of interest to investigate the point further, with a view to seeing how far it is a characteristic feature of density curves. The one molecule relation is also a very simple and obvious one, suggesting similar expressions for other salts.

Of the immense amount of data available on solution densities, we have found as a rule that either they extended over too short a range or the observations had been plotted, the curves smoothed out and the densities given at equal intervals. This made them of little value for reduction by the difference method used by us. It was necessary therefore for us to repeat a great deal of work that had already been done.

Our work has included a study of MgSO_4 , CdSO_4 , K_2SO_4 , Na_2SO_4 , $\text{Mg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, KNO_3 , NaNO_3 , NaCl , KCl , HCl ,

¹ Callendar and Barnes. Proc. Roy. Soc. 62, 117 (1897), afterwards given as loc. cit.

H_2SO_4 , and a verification of the ZnSO_4 results already obtained. We have not found that any of these curves show the flat part so strikingly as ZnSO_4 . We have found, however, distinct breaks in what are otherwise straight lines in our difference curves, which we cannot consistently smooth out. Without wishing to bring forward any "Hydrate theory", we are inclined to think that these peculiar "breaks" are probably caused by a change in the hydration of the salt, but in just what way we are not at present prepared to say. It is apparent that all the salts do not displace one molecule of water; some seem to displace two or three molecules, but not one less than one molecule. The relation can hardly be said to hold, however, in some cases.

Method and Accuracy of Work

Our method of measuring the densities is the most common and generally accepted one of filling a weighed "Ostwald" pyknometer. The capacity of our pyknometers we have restricted to 10 cc, as this enabled us to obtain an accuracy of one in ten thousand quite easily. Our weights were taken, however, to a tenth milligram, and it was found that no unusual care was required to enable the "fillings" to be made to two or three-tenths milligram. The capacity of the pyknometers was measured by weighing a number of times with air-free distilled water, and we found that after immersing in a constant temperature water-bath for fifteen or twenty minutes and drying so as to leave a maximum coating of water vapor on the glass we could obtain water equivalents to one or two-tenths milligram. The capacity was calculated assuming one cc of water to weigh one gram at 4°C .

The constant temperature water-baths already described¹ were of great assistance in the present work. Always before filling the pyknometers they were immersed in the bath for a short time so that when they were taken out and wiped dry they were in the same condition for weighing as when filled with solution. After obtaining their weights they were quickly filled with solution nearly to the mark and again immersed in the water-bath.

¹ Loc. cit. p. 119.

Only a very small quantity of solution was then required to fill them to the mark after which they were wiped dry and weighed. For refilling they were washed out with water and alcohol and dried in a current of hot air.

The chemical analysis of the saturated solutions was by far the most uncertain of our determinations. We thought for this reason that the great refinement obtained in density determinations, which seems to be limited only by the capacity and working convenience of the pyknometer, was quite unnecessary. Of course the relative values of our densities are not affected by a slight error in the determination of the concentration, but until the chemical methods are more refined and we are more certain of the atomic weights, there can be little value in measuring densities to six or seven decimal places.

Nearly all our salts used were Merck's standard and those that were not were purchased chemically pure. Saturated solutions were made by shaking an excess of salt with pure distilled water at room temperature, and filtering. After the strength of the saturated solution was determined the dilutions were made by weighing out amounts of the main solution in a corked test-tube, and then weighing the quantity of added water. As soon as this complete weight was obtained the mixture was carefully stirred by means of a flattened glass rod, without outward agitation, and then sucked up into the pyknometer. The dilutions ranged from $\frac{1}{2}$ to 100 volumes of water.

All the distilled water used was rendered air-free through exhaustion by a water pump under a layer of heavy paraffin oil. We found it very necessary to do this as otherwise there was quite a serious accumulation of air bubbles on the inside surface of the pyknometers. By using from eight to ten pyknometers and weighing out a number of dilutions one after the other, it was possible to proceed with considerable rapidity, the only limit being the time taken with the chemical analysis.

The method of reducing the observations is the same as that already described.¹ The percent strength of the

¹ Loc. cit. p. 142.

solution p , obtained by a chemical analysis, was multiplied by the observed density d and the product divided by 100, giving the volume concentration w in grams per cc. By adding to the weight of one cc of water, at the temperature of the observed density, the weight of the salt w , the density of the solution was obtained assuming there was no change in volume. By subtracting the observed density from this a series of differences was obtained which we have plotted against the volume concentration.

We have, besides obtaining the observations about to be described, reduced the observations of a number of other observers on the same plan and have found with a few marked exceptions a very good agreement with our own. We find however that the expression of density is rather an arbitrary matter and that some have given not the true density which is defined as

$$\frac{\text{Mass}}{\text{volume}}$$

but a density in terms of water at the temperature of the experiment. In most cases of course the observer has stated that the density is in terms of water, but it appears to us that a stricter adherence to the true meaning of density would be desirable.

Observations

We have arranged our results in tabular form and have plotted the values of w and $(wt. \text{ of water} - w) - d$. The position of the dotted points, which represent the observations on the plot, will give quickly the divergence from a one, two or three molecule relation, represented by a straight line, either from the origin or a point along the w axis. The abscissae represent values of w , while the ordinates, values of the difference. In the tables we have put in the first column the values of p the percentage strength of solution. In column two are the observed values of the density d , made at a temperature t° . Column three contains the values of $\frac{pd}{100}$ or w . The calculated density is placed in column four, obtained by adding to the weight of

Fig. 1

one cc of water at t° , the weight of salt w . In five the difference between the calculated and observed density; and in six a calculated difference is put representing either a one, two or three molecule relation. In plotting it has been necessary to cramp the curves somewhat, but the general relations may be very clearly seen. It will be noticed at once that the molecule relation is by no means an accurate one for all the salts, although it holds for a few with surprising closeness. The peculiar break in the curves is unmistakable. In some cases the density curve appears to start out to follow a one molecule relation and then bends to a two molecule, or starting with a two molecule bends to a three. We cannot conscientiously draw curves, other than straight lines, through the observations plotted in Fig. 1, but in

Fig. 2

Fig. 2 it appears that the sulphates of magnesium, cadmium and zinc would be best represented by a parabolic curve.

Objections have been raised repeatedly to the idea of breaks occurring in density curves on the ground that if they were due to hydration the change would take place gradually and not suddenly.¹ Of course we do not suppose that any transition occurs

¹ Nernst. Theor. Chemie, 420.

with abruptness, but that there is a rounding off of the meeting-point of the otherwise straight lines. There is no doubt whatever that the change of hydration with temperature occurs with great abruptness¹ and there seems hence very little reason not to suppose that a similar change with concentration might occur. As we have already said, however, we do not wish to bring forward any hydrate theory but merely to give our experimental results.

TABLE I

ZnSO_4		$t^\circ = 18.5^\circ$		$M = 161$	
p	d	w	$0.9985 - w$	$(0.9986 - w) - d$	$\frac{18}{161} (w - 0.150)$
29.22	1.3718	0.40057	1.3992	0.0274	0.0280
25.14	1.3091	0.32910	1.3277	0.0186	0.0200
21.28	1.2528	0.26659	1.2652	0.0124	0.0130
17.08	1.1957	0.20422	1.2028	0.0071	0.0061
11.20	1.1220	0.12567	1.1243	0.0023	0.0000
8.44	1.0894	0.09195	1.0906	0.0012	0.0000
6.65	1.0696	0.07112	1.0697	0.0001	0.0000
3.82	1.0387	0.03968	1.0383	-0.0004	0.0000
3.18	1.0318	0.03281	1.0314	-0.0004	0.0000
1.46	1.0138	0.01480	1.0134	-0.0004	0.0000
0.577	1.0045	0.00580	1.0044	-0.0001	0.0000

TABLE II

MgSO_4		$t^\circ = 18.2^\circ$		$M = 120$	
p	d	w	$0.9987 - w$	$(0.9987 - w) - d$	$\frac{18}{120} (w - 0.060)$
26.25	1.2903	0.3387	1.3374	0.0471	0.0419
25.91	1.2860	0.3332	1.3319	0.0459	0.0410
24.53	1.2693	0.3114	1.3101	0.0408	0.0377
21.60	1.2350	0.2663	1.2650	0.0320	0.0312
18.41	1.1950	0.2200	1.2187	0.0237	0.0240
13.79	1.1423	0.1575	1.1562	0.0139	0.0146
12.63	1.1292	0.1426	1.1413	0.0121	0.0124
11.29	1.1147	0.1259	1.1246	0.0099	0.0099
8.08	1.0803	0.0872	1.0859	0.0056	0.0041
2.01	1.0187	0.0204	1.0191	0.0004	0.0000

¹ Ernst Cohen. Zeit. phys. Chem. 14, 53 (1894); loc. cit. p. 150.

TABLE III

CdSO ₄		$t = 18.2^\circ$		M = 208	
p	d	w	$0.9987 - w$	$(0.9987 - w) - d$	$\frac{18}{208}(w - 0.0701)$
39.86	1.5639	0.6231	1.6218	0.0579	0.0477
31.53	1.4080	0.4439	1.4426	0.0346	0.0324
26.85	1.3310	0.3574	1.3561	0.0251	0.0248
24.17	1.2901	0.3118	1.3105	0.0204	0.0209
18.35	1.2084	0.2217	1.2204	0.0120	0.0132
13.27	1.1437	0.1518	1.1505	0.0068	0.0071
9.97	1.1045	0.1102	1.1089	0.0044	0.0035
7.46	1.0764	0.0803	1.0790	0.0026	0.0009
6.12	1.0619	0.0650	1.0637	0.0018	0.0000
2.52	1.0242	0.0259	1.0246	0.0004	0.0000
1.45	1.0132	0.0147	1.0134	0.0002	0.0000
0.464	1.0033	0.0046	1.0033	0.0000	0.0000

TABLE IV

K ₂ SO ₄		$t = 20.1^\circ$		M = 174	
p	d	w	$0.9983 - w$	$(0.9983 - w) - d$	$\frac{36}{174}w$
9.83	1.0800	0.10615	1.1045	0.0245	0.0219
8.172	1.0657	0.08708	1.0854	0.0197	0.0180
6.779	1.0539	0.07144	1.0697	0.0158	0.0148
5.021	1.0394	0.05218	1.0505	0.0111	0.0108
3.127	1.0238	0.03202	1.0303	0.0065	0.0066
2.508	1.0186	0.02554	1.0238	0.0052	0.0053
1.448	1.0100	0.01463	1.0129	0.0029	0.0030
1.079	1.0070	0.01087	1.0092	0.0022	0.0022
1.047	1.0066	0.01053	1.0088	0.0022	0.0022
0.455	1.0018	0.00456	1.0029	0.0011	0.0009

TABLE V

Na ₂ SO ₄		$t = 17.5^\circ$		M = 142	
p	d	w	$0.9989 - w$	$(0.9989 - w) - d$	$\frac{18}{142}w$
13.06	1.1226	0.14662	1.1453	0.0227	0.0185
11.75	1.1094	0.13043	1.1291	0.0197	0.0165
10.68	1.0990	0.11737	1.1161	0.0171	0.0148
8.544	1.0784	0.09214	1.0908	0.0124	0.0117
6.762	1.0615	0.07178	1.0705	0.0090	0.0091
4.015	1.0358	0.04159	1.0403	0.0045	0.0053
2.599	1.0225	0.02658	1.0253	0.0028	0.0034
2.375	1.0204	0.02423	1.0229	0.0025	0.0030
1.818	1.0154	0.01846	1.0172	0.0018	0.0023
1.349	1.0109	0.01364	1.0123	0.0014	0.0017
0.5204	1.0037	0.00522	1.0039	0.0002	0.0006
0.2921	1.0014	0.00293	1.0016	0.0002	0.0004

TABLE VI

KCl		$t = 20.1^\circ$		$M = 74.6$	
p	d	w	$0.9983 + w$	$(0.9983 - w) - d$	$\frac{36}{74.6} w$
36.43	1.1853	0.43171	1.4300	0.2447	0.2083
31.12	1.1554	0.35954	1.3578	0.2024	0.1735
24.79	1.1215	0.27887	1.2772	0.1557	0.1345
18.06	1.0866	0.19610	1.1944	0.1078	0.0945
13.17	1.0617	0.13980	1.1381	0.0764	0.0675
8.412	1.0386	0.08736	1.0857	0.0471	0.0421
6.610	1.0297	0.06806	1.0664	0.0367	0.0328
4.419	1.0193	0.04505	1.0433	0.0240	0.0218
3.456	1.0148	0.03507	1.0334	0.0186	0.0169
1.197	1.0040	0.01202	1.0103	0.0063	0.0058

TABLE VII

NaCl		$t = 18.0^\circ$		$M = 58.5$	
p	d	w	$0.9987 + w$	$(0.9987 - w) - d$	$\frac{18}{58.5} w$
25.37	1.1928	0.30263	1.3013	0.1085	0.0930
21.25	1.1592	0.24637	1.2451	0.0859	0.0756
17.35	1.1277	0.19563	1.1943	0.0666	0.0602
13.25	1.0958	0.14518	1.1439	0.0481	0.0446
9.34	1.0665	0.09960	1.0983	0.0318	0.0306
4.810	1.0332	0.04969	1.0484	0.0152	0.0153
2.991	1.0202	0.03052	1.0292	0.0090	0.0094
2.593	1.0173	0.02638	1.0251	0.0078	0.0081
1.746	1.0111	0.01765	1.0164	0.0053	0.0054

TABLE VIII

KNO ₃		$t = 20.1^\circ$		$M = 101.1$	
p	d	w	$0.9983 + w$	$(0.9983 - w) - d$	$\frac{36}{101.1} w$
25.54	1.1783	0.30095	1.2993	0.1210	0.1072
21.95	1.1510	0.25270	1.2510	0.1000	0.0900
17.88	1.1200	0.20033	1.1986	0.0786	0.0713
13.93	1.0913	0.15203	1.1503	0.0590	0.0541
8.706	1.0553	0.09186	1.0902	0.0349	0.0327
5.393	1.0331	0.05571	1.0540	0.0209	0.0198
4.389	1.0264	0.04506	1.0434	0.0170	0.0160
2.848	1.0165	0.02895	1.0273	0.0108	0.0103
2.030	1.0113	0.02053	1.0188	0.0075	0.0073
0.741	1.0030	0.00743	1.0057	0.0027	0.0027

TABLE IX

NaNO_3		$t = 20.1^\circ$		$M = 85$	
p	d	w	$0.9983 + w$	$(0.9983 + w) - d$	$\frac{36}{85} w$
42.05	1.3380	0.56267	1.5609	0.2229	0.2383
35.65	1.2765	0.45510	1.4534	0.1769	0.1927
31.72	1.2407	0.39365	1.3919	0.1512	0.1667
23.24	1.1696	0.27180	1.2701	0.1005	0.1151
17.370	1.1228	0.19505	1.1933	0.0705	0.0826
11.915	1.0819	0.12888	1.1272	0.0453	0.0545
9.665	1.0656	0.10300	1.1013	0.0357	0.0436
7.039	1.0468	0.07369	1.0730	0.0262	0.0312
4.241	1.0273	0.04357	1.0418	0.0145	0.0184
1.589	1.0096	0.01604	1.0143	0.0047	0.0068

TABLE X

$\text{Mg}(\text{NO}_3)_2$		$t = 20.1^\circ$		$M = 148$	
p	d	w	$0.9983 + w$	$(0.9983 + w) - d$	$\frac{54}{148} (w - 0.030)$
35.62	1.3110	0.46695	1.4653	0.1543	0.1594
31.15	1.2655	0.39420	1.3925	0.1270	0.1329
25.03	1.2057	0.30172	1.3000	0.0943	0.0990
19.55	1.1551	0.22585	1.2242	0.0691	0.0713
13.43	1.1028	0.14815	1.1465	0.0437	0.0432
10.09	1.0753	0.10850	1.1068	0.0315	0.0287
6.650	1.0480	0.06968	1.0680	0.0200	0.0145
4.672	1.0330	0.04826	1.0466	0.0136	0.0066
4.001	1.0276	0.04112	1.0394	0.0118	0.0041
1.372	1.0085	0.01383	1.0121	0.0036	0.0000

TABLE XI

$\text{Zn}(\text{NO}_3)_2$		$t = 17.3^\circ$		$M = 189$	
p	d	w	$0.9988 + w$	$(0.9988 + w) - d$	$\frac{36}{189} w$
47.28	1.5504	0.73310	1.7319	0.1815	
41.32	1.4579	0.60240	1.6012	0.1433	
30.86	1.3136	0.40535	1.4042	0.0906	
29.21	1.2933	0.37780	1.3766	0.0833	
19.65	1.1830	0.23246	1.2313	0.0483	
14.39	1.1284	0.16232	1.1611	0.0327	
11.36	1.0988	0.12478	1.1236	0.0248	0.0238
7.091	1.0597	0.07515	1.0740	0.0143	0.0143
5.923	1.0491	0.06213	1.0609	0.0118	0.0118
1.574	1.0118	0.01593	1.0147	0.0029	0.0030
1.210	1.0087	0.01221	1.0110	0.0023	0.0023

TABLE XII

MgCl_2		$t = 20.1^\circ$		$M = 95.0$	
p	d	w	$0.9983 - w$	$(0.9983 - w) \cdot d$	$\frac{18}{95} w$
28.83	1.2569	0.36237	1.3607	0.1038	
25.59	1.2241	0.31327	1.3116	0.0875	
20.31	1.1735	0.23842	1.2367	0.0632	
15.79	1.1324	0.17877	1.1771	0.0447	
10.185	1.0833	0.11033	1.1086	0.0253	
8.058	1.0650	0.08583	1.0841	0.0191	0.0163
5.919	1.0473	0.06198	1.0603	0.0130	0.0117
3.913	1.0304	0.04022	1.0385	0.0081	0.0076
3.903	1.0240	0.03210	1.0304	0.0064	0.0061
1.743	1.0126	0.01765	1.0160	0.0034	0.0033

TABLE XIII

HCl		$t = 19.5^\circ$		$M = 36.5$	
p	d	w	$0.9983 - w$	$(0.9983 - w) \cdot d$	
36.00	1.1818	0.4255	1.4238	0.2420	
29.97	1.1511	0.3450	1.3433	0.1922	
24.35	1.1207	0.2729	1.2712	0.1505	
18.55	1.0910	0.2024	1.2007	0.1097	
12.22	1.0587	0.1294	1.1277	0.0690	
9.148	1.0433	0.0954	1.0937	0.0504	
6.559	1.0305	0.0676	1.0659	0.0354	
3.540	1.0159	0.0360	1.0343	0.0184	
5.345	1.0246	0.0548	1.0531	0.0285	
1.356	1.0051	0.0136	1.0119	0.0068	

TABLE XIV

H_2SO_4		$t = 19.4^\circ$		$M = 98.0$	
p	d	w	$0.9983 - w$	$(0.9983 - w) \cdot d$	
94.10 ¹	1.8380	1.7295	2.7278	0.8898	
84.59	1.7998	1.5223	2.5206	0.7208	
73.08	1.6743	1.2235	2.2218	0.5475	
61.35	1.5341	0.9412	1.9395	0.4054	
40.72	1.3220	0.5383	1.5366	0.2146	
31.94	1.2430	0.3970	1.3953	0.1523	
23.77	1.1747	0.2792	1.2775	0.1028	
14.72	1.1023	0.1623	1.1606	0.0583	
9.802	1.0670	0.1046	1.1029	0.0359	
4.826	1.0320	0.0498	1.0481	0.0161	

¹ A rough approximation taken from density tables, which will be quite sufficient to give a general idea of the way in which the difference curve follows the rate of dilution.

Zinc Sulphate

In Table I will be found the observed densities and the differences assuming a one molecule relation starting from a density of 1.150. The plot in Fig. 2 will perhaps show this more clearly. The rounded points show the observations from Table I, while the crosses show the original observations already described.¹ The peculiar feature is the sharp bend towards the origin, causing the curve to pass in along the axis of w . There is certainly no abrupt change here, but just what the explanation is we are not yet able to say. We hope, however, soon to be able to do so. We have made density determinations at 0° and find that the effect is to lower all the points and cause the flat part to be much more exaggerated, that is to make the curve run into the axis of w much sooner. Determinations at 35° show the curve higher and passing into the origin apparently without any flat part. The scale commences four divisions from the extreme left and for the horizontal axis is two and one-half divisions to $w = 0.100$. The vertical scale is two and one-half divisions to $\text{diff.} = 0.0100$.

Magnesium Sulphate

Table II and Fig. 2 give the observations and plot of this salt. The flat part is not nearly so marked as for zinc. The one molecule relation holds very closely until the more concentrated or more nearly saturated solutions when the divergence is quite marked. We have drawn the one molecule line from a density of 1.060. The density of solutions of MgSO_4 may be quite accurately estimated from the following linear expression

$$d_{18} = 0.9987 + w - \frac{18}{120} (w - 0.060).$$

The scale for the plot commences at the extreme left, but otherwise is the same as for ZnSO_4 .

Cadmium Sulphate

Table III, Fig. 2. The divergence from the one molecule

¹ Loc. cit. p. 142.

relation is more marked in the case of strong solutions of CdSO_4 , but holds with remarkable closeness for dilute solutions. The flat part is quite clearly shown in the plot. The scale commences at the extreme left as for MgSO_4 , but differs from that salt and ZnSO_4 on the vertical axis by having only two divisions to the diff. = 0.010. The horizontal scale is the same as for MgSO_4 . The expression for the density is in every way similar to the ones for Mg and Zn, substituting, of course

$$-\frac{18}{208} (w - 0.070).$$

Potassium and Sodium Sulphates

Tables IV and V, Fig. 1. These sulphates are plotted to the same scale and show a close similarity except that the potassium salt follows more nearly a two molecule relation while sodium follows a one. One decided break occurs in each density line, and this is brought out clearly in the plot. The calculated difference column shows this break by diverging from the observed difference column at a density of 1.0539 in the case of K_2SO_4 and for NaSO_4 at 1.0990. Similar density expressions may be given for these two salts, as have already been cited.

Potassium and Sodium Chlorides

Tables VI and VIII, Fig. 1. These salts are also plotted to the same scale, commencing five divisions to the right of the sulphate curves. Like K_2SO_4 , KCl follows the two molecule line, but shows no definite break. It is practically a straight line running in towards the origin. NaCl shows a bend and, like the sulphate, follows the one molecule line.

Potassium and Sodium Nitrates

Tables VIII and IX, Fig. 1. KNO_3 like KCl is almost a perfect straight line approximating to a two molecule slope. NaNO_3 , however, follows the two molecule line and in this respect differs from NaCl or Na_2SO_4 . A break occurs in the NaNO_3 curve at about $w = 0.20$.

Magnesium and Zinc Nitrates

Tables X and XI, Fig. 1. Both these salts approximate to a three molecule relation, but in the case of $\text{Zn}(\text{NO}_3)_2$ we have not considered it necessary to put in the three molecule differences in the table, merely wishing to show the remarkable agreement of the two molecule differences for the more dilute solutions and the position of the well defined break. The vertical scale is the same in the plot for both salts. The horizontal scale begins for $\text{Zn}(\text{NO}_3)_2$ three divisions to the right and is represented by one division = 0.20.

Magnesium Chloride

Table XII, Fig. 1. MgCl_2 follows for dilute solutions the one molecule relation shown by the difference column in the table. At a value of $w = 0.10$, however, a decided bend occurs, causing the differences to approximate more nearly to a two molecule line. The vertical scale is numbered to the right and is represented by two and one-half divisions to 0.10. The horizontal scale commences six divisions to the right and is one division to 0.10.

We have, besides studying the salts already mentioned, determined the densities of pure HCl and H_2SO_4 to see if any relationship existed between the pure acids and the salts. Tables XIII and XIV give the results of these observations, but we have not considered it necessary to plot them. The difference curve for HCl follows approximately a one molecule relation and apparently is a straight line passing into the origin without a break. The difference curve for H_2SO_4 shows a certain similarity to the sulphates of cadmium, magnesium and zinc. Whether the observations should be smoothed out into a parabolic curve or whether they would be more nearly represented by a number of straight lines, as was pointed out by Mendeleejew,¹ we are not at present prepared to say. Plotting the observations on a large scale and feeling assured as we do that the densities are accurate

¹ Zeit. phys. Chem. 1, 273 (1887).

to one in ten thousand, we are inclined to doubt whether we could conscientiously smooth out the points. There is a slight indication also of a flat part similar to that shown in the sulphates of Cd, Mg and Zn.

It is not altogether clear whether the similarity in density changes should be looked for in salts with a common acid or with a common base. From the study of the K and Na salts, with the exception of NaNO_3 , it looks as though similar relations might be expected from a common base. On the contrary, from the results of H_2SO_4 and the sulphates of Mg, Cd and Zn, it looks like a similarity in a common acid radical. It is exceedingly unlikely, however, that we can find any simple expression for the change of density with strength of solution that will hold for all salts. The secondary reactions of the salt on the water solvent and the anomalous changes possibly produced by the different degrees of dissociation make the question a difficult one. We would have wished to give more extended work here for some of the organic salts and with different solvents, but unfortunately the stress of other and more important work, as well as the lack of time allotted for the present work have prevented.

McDonald Physical Laboratory, McGill University, Oct. 12, 1898